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In situ transmission electron microscopy analyses of thermally annealed self catalyzed GaAs nanowires grown by molecular beam epitaxy

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Abstract. Self catalyzed GaAs nanowires grown on Si-treated GaAs substrates were studied with a transmission electron microscope before and after annealing at 600°C. At room temperature the nanowires have a zincblende structure and are locally characterized by a high density of rotational twins and stacking faults. Selected area diffraction patterns and high-resolution transmission electron microscopy images show that nanowires undergo structural modifications upon annealing, suggesting a decrease of defect density following the thermal treatment.

Introduction

GaAs nanowires (NWs) grown by catalyst assisted methods are typically affected by the presence of structural defects. Stacking faults are common, and the two GaAs polytypes, zincblende (ZB) and wurtzite (WZ) are often intermixed along the growth axis of a single nanowire. The two GaAs polytypes of GaAs have indeed a small cohesive energy difference (24 meV per III-V atom pair [1]). The occurrence of one or the other of the possible stacking has been recently predicted on thermodynamic basis in terms of the relative weight of the surface energies of the different phases involved in the NW growth, i.e. solid, liquid and gaseous [2]. Recently, wide effort has been devoted to carefully tune the growth conditions in order to obtain pure ZB or pure WZ NWs [3, 4]. Self-catalyzed NWs typically display ZB structure but twins and stacking faults are generally present [5]. We give here a preliminary account of a study of the thermal stability of self-catalyzed GaAs NWs, especially with respect to the stability of stacking faults.

Experimental details

NWs have been synthesized by solid source molecular beam epitaxy using a Riber 32P apparatus: (111)B GaAs wafers have been deoxidized and 3-4 monolayers of Si (1 monolayer = 1.36 Å) have been epitaxially deposited. Air exposure and outgassing in ultra high vacuum completed the substrates preparation for self catalyzed NW growth [6]. NWs were grown at a growth temperature of 620°C with an As to Ga beam-equivalent pressure ratio of 12. In these growth conditions a two-dimensional growth rate of 1 µm/hour is observed. A suspension of the as-grown nanowires in ethanol produced by sonication was then applied to a nickel Quantifoil TEM grid and examined in the transmission electron microscope (Tecnai G2 operating at 200 keV). The annealing step consisted of 10 minutes at 600°C inside the TEM chamber using a sample holder with a platinum heating element (Gatan Inc.). High temperature measurements were possible only in diffraction mode, while for high resolution the absence of thermal drift was mandatory: to acquire high resolution images, then, 30 minutes were waited after the

annealing.

Results and discussion

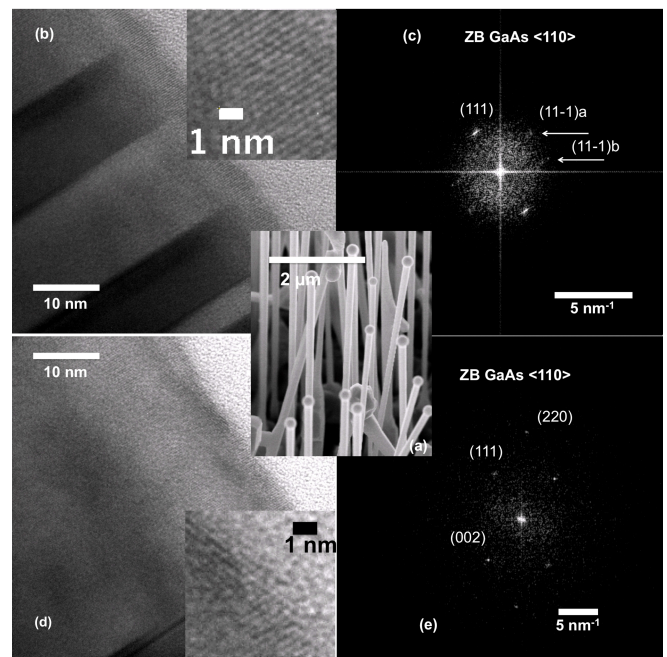


Fig. 1. (a) SEM image of GaAs NWs on (111)B GaAs substrates as grown. (b) HRTEM image of a NW in the ZB region at the base; (c): filtered FFT of (b); (d): HRTEM image of the same NW after the annealing step; (e) filtered FFT of (d). The insets in (b) and (d) show details of the crystal lattice. Notice that the FFTs are aligned with the HRTEM images.

In fig. 1 the result of the annealing step on the NW body where it had pure ZB crystal structure is visible. In Fig. 1(a) a scanning electron microscope image of the NWs as grown on the (111)B GaAs substrate. In 1(b) the NW body with twinned zones of alternating contrast along the growth axis. The inset in 1(b) and the fast Fourier transform (FFT) of the image, visible in 1(c), confirms the stacking to be ZB, diffraction spots are indexed according to this

structure. In 1(d) the HRTEM image of the same NW shows a greater uniformity possibly due to a tilt of the crystal after the annealing step, though the detail of the atomic lattice is still visible in the inset. In 1(e) the FFT of 1(d): spot indexes show the stacking to be ZB. Notice that the FFTs in 1(c) and 1(e) are aligned with the HRTEM image.

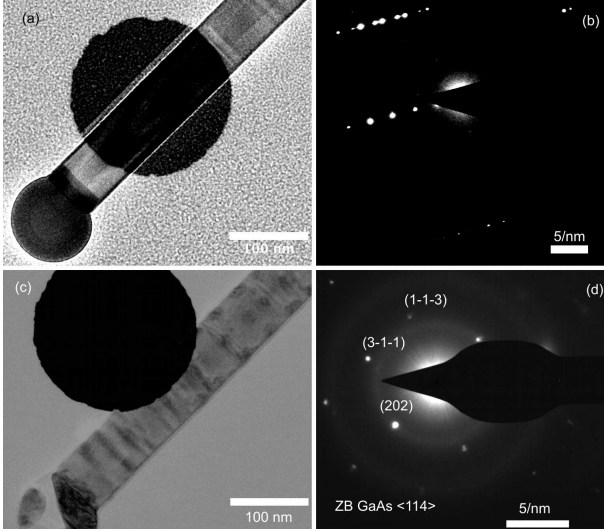


Fig. 2. Low magnification TEM images (left) and corresponding SAD patterns taken from the black circled zone (right) of a NW before (top) and after (bottom) the annealing step. Notice the black spots on the NW body in the region next to the SAD aperture in (c)

In fig. 2 the low magnification image of a NW tip is visible, before in 2(a) and after in 2(c) the annealing step. In both 2(a) and 2(c), the black circle region shows where the SAD pattern in 2(b) and 2(d), respectively, were taken; notice that the diffractograms in 2(b) and 2(d) are 90° rotated with respect to 2(a) and 2(c). The diffractogram in 2(b) is compatible with a defected region with stacking faults and/or rotational twins, whereas the diffractogram in 2(d) is much simpler and strongly suggests the absence of multiple crystal phases in that area. Although a slight movement or rotation of the NW as result of the annealing step (same as previous image) could be the reason of the disappearance of some diffraction spots, distances and positions of the main diffraction peaks show pure ZB phase in the selected area. It should be pointed out that the slight different selected area between 2(a) and 2(c) is a result of the thermal drift at high temperature. Fig 2(c) shows other particulars, if compared with 2(a): first, the Ga nanoparticle on top of the NW has a different morphology; second, the presence of greater contrast spots on the NW body, close to the selected area, suggests a partial dewetting of the Ga nanoparticle. In this case, Ga atoms have migrated down the NW body and segregated in smaller Ga clusters; this should be taken into account in considering transport or electronic properties of annealed NWs. Their position inside the NW body couldn't though be resolved by this TEM analysis.

With an energy difference of 24 meV per III-V atom pair between ZB and WZ GaAs polytypes and thermal energy employed for these experiments of 75 meV, structural changes in NWs are very likely to be triggered.

Conclusions

These preliminary results show that structural changes take place when self catalyzed GaAs NWs undergo thermal annealing. In particular, where the stacking was ZB, it remains ZB and where the structure was defected it seems to become simpler towards pure ZB. The incidental evidence of Ga diffusion within the NW body moreover confirms the effectiveness of post growth annealing procedures to affect NW structure. An annealing step in As atmosphere inside the growth chamber after the growth interruption and other TEM analyses performed with a lower electron beam energy are upcoming points of this investigation.

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